EVIDENCE FOR A SECOND GENERATION OF MAGNESITE IN MARTIAN METEORITE ALLAN HILLS 84001.

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Introduction: Single-stage formation mechanisms for carbonate and other secondary minerals in ALH84001 are rapidly being revised to include multiple stages of carbonate growth and later thermal and mechanical events including alteration [1-9]. In an effort to confirm some of these more complex histories we have been studying carbonate-bearing regions within this meteorite. Magnesitic carbonates found in contact with unique "slab" carbonates [9] in two thin sections of ALH84001 show indications of being of a later generation. The results of our observations help clarify the origins of the carbonate and related minerals in ALH84001, and how these minerals can be used to understand the history of interactions between the martian crust and its volatile inventory.

Methods: Textural and fracture analyses of carbonates were performed both petrographically and using backscatter electron images (BSE). These BSE images and additional compositional analyses were obtained using the Cameca SX-50 electron microprobe at the University of Chicago.

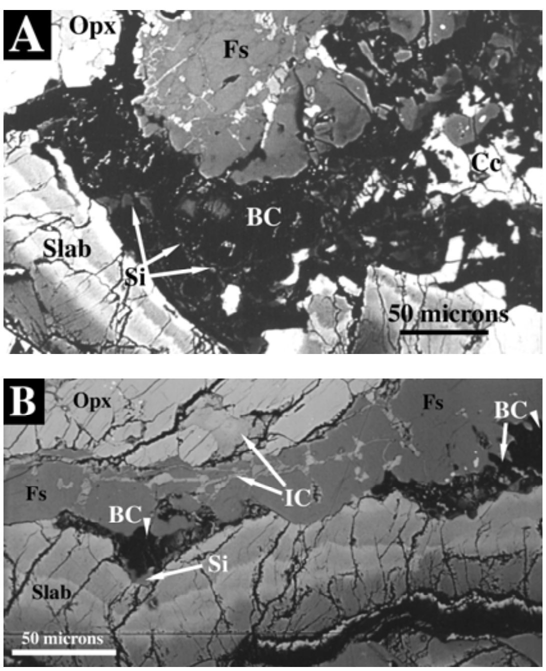

Figure 1. Black carbonates (BC) in **(A)** ALH84001,302 and **(B)** ALH84001,303 surrounded by carbonates (IC) interstitial to feldspathic glass (Fs) orthopyroxene (Opx), feldspathic glass (Fs), slab carbonates (Slab) and silica glass (Si). (A) has been contrast enhanced to better show silica glasses.

Texture: The regions studied contain near Mg-end-member carbonate material that is texturally distinct from carbonate in rosettes or slabs (Fig. 1). We refer to these carbonates, whose low Ca and Fe abundance cause them to appear black in BSE images, as "black carbonates" to distinguish them from the Mg-rich carbonates in the alternating magnesite-siderite-magnesite (MSM) layers found on the exteriors of slabs and rosettes.

Evidence that these carbonates are distinct from rosettes or slabs is especially visible in ALH84001,302 (Fig. 1), where black carbonate fills most of the space between slab carbonates and feldspathic glass. These black carbonates occur as numerous small grains or blebs, semi-circular in cross section. They show no evidence of being the outer edges of rosettes, as they are smaller (~50 microns) and more uniform in size than rosettes (~100-250 microns)[1]. These may be similar to carbonates described in [10].

Black carbonates have a different fracturing habit than do rosettes or slab carbonates. Fractures tend to form around individual blebs, with only a few fractures crossing blebs. Black carbonates are less fractured than rosettes and slab carbonates but more fractured than feldspathic glasses.

Black carbonates have an unusual relationship with silica glass similar to that noted by [11]. In some cases, as in ALH84001,302 (Fig. 1), silica glass is only present associated with fractures around black carbonate blebs and often forms rims around the blebs. In other cases, silica glass occurs as larger blebs (roughly 100 by 100μm) surrounded by black carbonates.

Chemistry: Black carbonates have predominantly Mg-rich compositions. Black carbonate spans a wider compositional range than do magnesites in the MSM layers, stretching from nearly pure $MgCO_3$ toward more intermediate compositions. Microprobe analyses of black carbonates show no recognizable zoning or other chemical trends. Compositions do not vary with respect to distance from any particular center point nor do they vary dependent on proximity to other mineral phases.

Formation Sequence: Black carbonates almost certainly formed *after* the formation and fracturing of slab carbonates and rosettes (including the MSM layers) as most fractures crossing slab carbonates do not into black carbonates. Black carbonates also entrain slab carbonates material in some cases.

Unlike MSM magnesites, black carbonates are found in contact with what we believe are the oldest, Ca-rich slab carbonate surfaces. These Ca-rich interiors, that nucleated onto other surfaces, had to have been exposed and space made available prior to black carbonate formation. In both regions studied, carbonate nucleation surfaces were peeled from their original surfaces allowing black carbonate to precipitate.

Though fracture analysis is inconclusive, black carbonates being physically intimately mixed with silica glasses suggests that the two phases formed or were emplaced during the same event. The fact that neither silica glass nor black carbonates intrudes into slab carbonates, rosettes or feldspathic glass, though they are both found in contact with these other phases, supports their having formed simultaneously. Recent oxygen isotope analyses from [12] suggest that carbonate and silica glasses in their study regions did not form in equilibrium, but the carbonate they are discussing cannot be linked to our black carbonates.

The bulk of evidence points toward black carbonates forming before feldspathic glass was mobilized. The occurrence of black carbonate on the edges of separated sections of slab carbonate in ALH84001,303 (Fig. 1b) indicate that it was precipitated before the slab was torn apart. There are numerous occurrences in both regions of black carbonate entrained by what appears to have been mobile feldspathic glass. In addition, there exist locations where fractures transcend the boundaries between both types of carbonate but do not cross into feldspathic glasses.

Alteration: Textures suggest that black carbonates were formed after the MSM sequences and before feldspathic glass intruded. Black carbonates form a significant volume of the material in these regions, particularly in ALH84001,302, so whatever event formed them is an important slice of ALH84001 history.

Black carbonate seems to be closely related to the magnesite in the MSM rims. Chemically, the two types of magnesite are similar, though black carbonate contains fragments of other phases. It is possible that the outer layer of the MSM sequence is actually of the same generation as black carbonates, especially since silica is associated with both of these phases. Alternatively, these two phases may in fact represent two stages of a single alteration event. The first of these alteration events would have formed the MSM rims, and the second would have precipitated black carbonates and silica glass, filling in the trend with compositions lost during the first alteration (possibly from cations dissolved into the fluid during the first event and later re-precipitated). If dissolved components from the MSM alteration event went into the fluid, but the fluid remained in the fractures, a later event may have caused the re-precipitation off these elements as black carbonates. An influx of silica-rich fluid during this or a later impact event may have been necessary to cause the precipitation of amorphous silica between rosettes and around the blebs of black carbonate. Though there is evidence that black carbonate and silica glass formed isotopic analysis of black carbonate and silica glasses should shed more light on the relationship between these phases.

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